Indian Journal of Chemical Technology
Vol. 27, May 2020, pp. 210-218

Modelling of heat integrated reactive distillation column (r-HIDiC): Simulation studies of MTBE synthesis

S A Ahmed* & S A Ahmad

Department of Chemical Engineering, Aligarh Muslim University, Aligarh-20200 India
E-mail: ahmedsofia15@gmail.com

Received 2 April 2019; Accepted 30 January 2020

In the present study, heat integrated distillation column is modelled and simulated for the production of Methyl tert-Butyl Ether (MTBE) from methanol and isobutylene using ASPEN Plus®. Also, the objective of this study is to have comparative analysis between the reactive distillation process and an alternative intensified process (r-HIDiC) to produce MTBE.

Rigorous simulation study has been conducted to compare the optimal flow sheet of the above two designs. Temperature and composition profiles are studied and compared for both the models and found that the temperature at the last stage of the stripping section in r-HIDiC is 406 K while that of the stripping section in RDC is 427.24 K. This reduced temperature decreases the composition of methanol in bottom product in stripping column in case of r-HIDiC as methanol forms a homogenous azeotrope with MTBE at 408.53 K. Also, it is found that, although with nominal increase in TAC i.e. 16.56%, in r-HIDiC design as compared to the reactive distillation column design which is caused due to the high cost of the additional compressor needed in the vapour compression, however, the r-HIDiC design can save reboiler and condenser heat duties to a considerable amount i.e. by 35.06% and 36.65% respectively.

Keywords: Heat Integrated Distillation Column, Process Intensification, Reactive Distillation.

The combined threat of increasing energy demands and costs, global warming and the increased dependence upon oil imported from politically unstable parts of the world have resulted in an interest in enhancing the thermodynamic efficiency of current industrial processes. Increasing energy efficiency in chemical processes not only provides economic benefits but also it leads to reduce the emissions resulting from the process operation. Distillation is perhaps the most important and widely used separation technique in the world today as it is used for 95% of all fluid separation in the chemical industry. Despite its apparent importance the overall thermodynamic efficiency of a conventional distillation is around 5-20%[1]. In order to improve the energy efficiency, the concept of process intensification was introduced to the distillation process in 1970[2].

The basic idea of heat integration is that the hot process streams are heat exchanged with cold process streams which results in a more economic use of resources. Consequently, many researches on the heat integrated distillation column (HIDiC) have been performed during the past few decades to investigate its feasibility and practicality in real world applications. These research has led to the creation of various improved distillation columns such as the Petlyuk column, divided-wall column, heat pump assisted column, diabatic distillation column, ideal HIDiC (i-HIDiC) and others. However, these columns have drawbacks in its applicability and exist only as simulation model[3].The HIDiC configuration has yet to be adopted by any industry but after successful pilot scale experimental studies undertaken by New-Energy and Industrial Technology Development Organization (NEDO), Japan; a joint venture between NEDO and TERI (The Energy & Resources Institute), India promises new projects in the field of process intensification at a conference held at New Delhi in January 2017.

This paper addresses a novel idea of process integration by combining reactive distillation and principles of heat integrated distillation column i.e. r-HIDiCthat allowed the synthesis of MTBE with significantly lower energy consumption. The synthesis of MTBE using reactive distillation scheme is in fact the most successful and largest application of process intensification[4]. However, the much needed attention to reduce the energy consumption and increase the efficiency of the existing reactive distillation column is studied in this work. Several

works have been carried out in recent years on the heat integration of reactive distillation column[5-7]. This work studied the performance of r-HIDiC and shows that the proposed scheme is thermodynamically feasible; also a comparative cost analysis for both schemes is also stated.

Modelling and Simulation

Process Description

MTBE synthesis process

For the study of simulation of reactive distillation and heat integrated reactive distillation, we have chosen MTBE production technique. MTBE is an organic compound manufactured via the chemical reaction of methanol and isobutene.

The reaction to produce MTBE is as given below:

$$CH_3C(CH_3)=CH_2+CH_3OH \leftrightarrow CH_3C(CH_3)OCH_3 \ldots(1)$$

Reaction kinetics has been taken from literature[8] and is given below:

$$r_{forward} = 3.67\times10^{12}\times\exp\left(-\frac{92440}{RT}\right)\frac{x_{IB}}{x_{MEOH}} \quad \ldots (2)$$

$$r_{backward} = 2.67\times10^{17}\times\exp\left(-\frac{134454}{RT}\right)\frac{x_{MTBE}}{x_{MEOH}^2} \quad \ldots (3)$$

Application of Process intensification

Reactive distillation process has been given special attention in the past two decades because of its potential for process intensification for certain types of chemical reactions. The major advantage of using this technology is combining the unit process and unit operation in a single column and thereby eliminating the separation step[9]. In a conventional distillation column, heat is supplied at the bottom reboiler and rejected at the top condenser, which means that the distillation process is actually operated by the degradation of energy from bottom to top. A straightforward approach to energy saving would involve transferring the heat rejected from the rectifying section to the stripping section of the same column. Such an approach, however, requires the heat rejected to be upgraded to a higher temperature level by compression. This can be achieved by various methodologies and one such method is studied in this work. In the HIDiC configuration, the heat transfer from the rectifying section to the stripping section leads the rectifying section to operate at higher pressure and temperature. The heat required to evaporate the liquid in the stripping section is obtained from the rectifying section, which decrease the energy charge on the reboiler. Despite an increasing interest in the heat integration techniques and in the column control, the novel idea of locating a reactive zone placed in the HIDiC column in the specified stage range leads to a significant reduction of the capital and operating costs by combining both reaction and distillation processes in a single vessel. In addition, applicability for mixtures with minimum and maximum boiling azeotrope can be processed in this configuration while reducing energy consumption.

Model development

In this study, simulation of distillation column which includes reactive distillation column and reactive heat integrated distillation column for production of MTBE with the help of ASPEN Plus®software is done. In reactive distillation column, both reaction and separation takes place simultaneously while in heat integrated distillation column the reactive step takes place in the stripping column.

Both the reactive and heat integrated (reactive stripper, non- reactive rectifier) schemes are modelled based on the following assumptions: the column operates in adiabatic condition with liquid phase, perfect mixing on the tray, negligible vapour holdup in any stage of the column, NRTL model (both for RDC and r-HIDiC), no reaction in the recovery column. Also; for the simplification of the modelling complexities, there are no hydrodynamic effects in the modelling work.

Simulation study

The simplified flow sheet for the reactive distillation process of producing MTBE is illustrated in Fig.1. The column configuration chosen in the current work have been studied previously[8,9]. The reaction between methanol and isobutene is carried out in reactive section of distillation column. The final components containing MTBE, unreacted methanol- isobutene mixture and inert n-butene is separated in the separating section of the column. Column separates MTBE in the bottom stream. The top stream originating from the column is condensed and inert n-butene is obtained as top product. A schematic diagram of the r-HIDiC concept is shown in Fig. 2. The internally heat-integrated design proposed in earlier studies[10]is used to develop r-HIDiC model. The number of stages for the reactive stripping section

and the rectifying section are assumed to be the same for the ease of construction. Due to the limitation on the operating pressure in the reactive stripping section where it has to be greater than 8 atm so that to avoid the occurrence of reversible reaction, the stripping column is operated at a pressure greater than 8 atm.

The heat integrated distillation column is simulated as two interconnected distillation columns using the RADFRAC block. Heat transfers between corresponding stages in the two sections were made by assigning side duties. Two typical heat distribution schemes, namely, uniform heat-transfer area and uniform heat distribution, were usually used in simulation studies of HIDiC[11]. The configuration in which the stripping section stages are thermally connected with the same number of stages in the rectifying section with uniform heat distribution is employed in the present work, as this was confirmed by previous studies[12] to be the most energy- efficient scheme for a propylene–propane splitter. The total amount of heat transferred between the two sections was adjusted to reduce the reboiler duty to less than 50 MW.

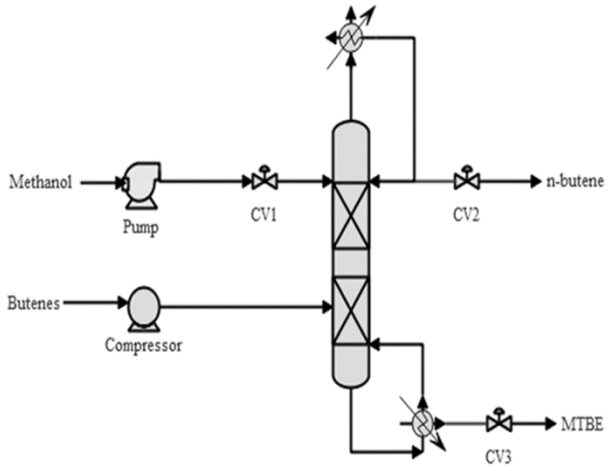

Fig. 1 — Conventional flow sheet for production MTBE.

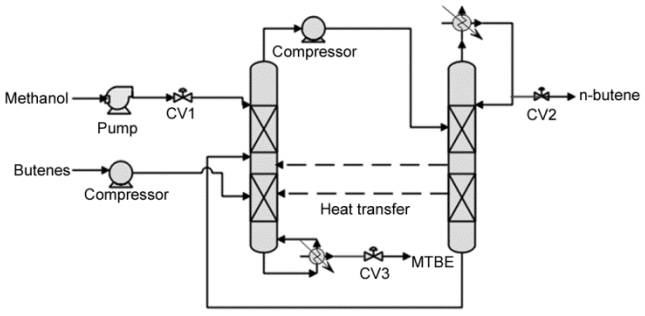

Fig. 2 — Conceptual design of the reactive heat integrated distillation system

The stripping section is charged with feed at two different locations, depending on where the reaction occurs. The top product of this section is fed to the rectifying section while the bottom of the rectifying section is recycled back to the stripping section. Product MTBE is obtained as bottom product from the reactive stripping section and inert n-butene is obtained from top product of the rectifying section.

Results and Discussion

Reactive distillation column

Column and feed specifications for reactive distillation column are shown in Table 1. The column consists of 16 stages including a total condenser and a partial reboiler. The column consists of three zones: rectification section stage 2, in which separation of inert (n-butene) takes place from unreacted components, reactive zone (3-6) in which methanol and isobutene react to form MTBE, stripping section (7-15) in which separation of product from unreacted components takes place. In the production of MTBE, the mole fraction of MTBE should be high in the bottom stream. Utilities used in the simulations is shown in Table 2.

Table 3 shows the results of the proposed model with published simulation results[8,9]. As it can be seen from Table 3, it is clear that the simulation results produced are quite similar to the published simulation results[4]. This similarity verifies that the proposed model is capable of successfully simulating catalysed

Table 1 — Design parameters of reactive distillation column

Column Configuration		Feed Specification		
Bottom flow rate (kmol/hr)	640.8	Parameter	Methanol	Butene
Reflux ratio	13	Feed stage	10	11
Column pressure (atm)	13	Feed temperature (K)	320	350
Pressure drop (atm)	0.5	Feed pressure (atm)	13	13
Liquid hold up (m^3)	3	Mole flow (kmol/hr)	711.3	1965.8
Number of reactive Trays	4	Composition	1	Iso-butene: 0.36
Number of trays	16			n-butene: 0.64

heterogeneous MTBE synthesis. It has been reported that a process utilising reactive distillation technology can boost the isobutene conversion up to 99% and higher[13]. With agreement to the reported isobutene conversion, simulation results showed an isobutene conversion of 97.94%, which is as desirable in real pilot plant reactive distillation column.

The temperature variation over the different stages of the column is shown in the Fig. 3. There are three stages in reactive distillation column. From the plot of temperature variation along the different stage of the column, we can say that the temperature in the column is increasing along the stages because of the increase in the concentration of the less volatile component that is MTBE (B.P.: 419.56 K at 13 atm). Also, owing to the fact that MTBE synthesis reaction is exothermic in nature and there is huge amount of heat evolved after reaction, it can be deduced that the temperature after the 6th reaction stage is increased exponentially with respect to each stage.

The results obtained for the concentration profile of all the components after simulating the column over the given data are shown in the Fig. 4. In the column the less volatile reactant (i.e. methanol) was fed at 10th stage and the more volatile reactant (i.e. butenes) at 11th stage to ensure high isobutene conversion. From the Fig. 4 it can be deduced that in the separation stage (7-15), the separation between unreacted methanol and product MTBE governs the purity of the product for the process.

Table 2— Basis for economic and equipment sizing

Energy cost ($/year)	LP steam = $7.78/GJ MP steam = $8.22/GJ HP steam = $9.88/GJ
Cooling water ($/year)	$0.354/GJ
Catalyst cost ($)	$10/kg
Electricity ($)	$0.0573 /kWh

If the reaction stages were increased from four stages, then the synthesis shift towards backward reaction as the synthesis reaction is reversible. Hence, the production of reactants is enhanced as per the reaction stoichiometry and the flow of MTBE in product stream is drastically reduced. However, when the number of stages was reduced from 15 stages; the mole flow of MTBE in bottoms was dropped. This could happen owing to the fact that at 7th stage the composition of MTBE is low and that of inert n-butene is high which further needs separation. Hence stages 7 to 15 act as a separation stage for n-butene/MTBE mixture.

Reactive- Heat Integrated Distillation Column

The relevant information about r-HIDiC is recorded in Table 4. The non-reactive rectifier that includes the trim-condenser and reactive stripper that combines the trim-reboiler consist of total 8 numbers of theoretical stages. The recycle stream mainly consisting of isobutene was fed at a stage (i.e., 5) so chosen based on reaction stoichiometry. At 4th stage

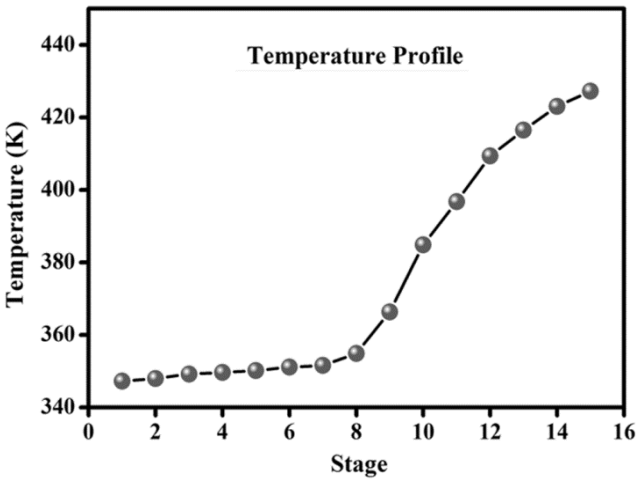

Fig. 3 — Temperature variation over the stages

Table 3 — Comparison of simulation results for operating conditions, feed and product Flow compositions

		Murat et al., 2003		Proposed Model	
Quantity	Units	Top	Bottom	Top	Bottom
x_{MeOH}		0.040	0.000	0.050	0.0018
x_{IB}		0.003	0.000	0.048	0.000
x_{MTBE}		0.000	0.960	0.000	0.987
$x_{n\text{-butene}}$		0.965	0.014	0.901	0.001
Temperature, *T*	K	348.8	423.8	347.22	427.25
Product Flow	kmol/h	1309.32	709.2	1406.13	640.8
IB conversion	Mole %	98.5		97.95	
MTBE Purity	Mole %	98.60		98.70	

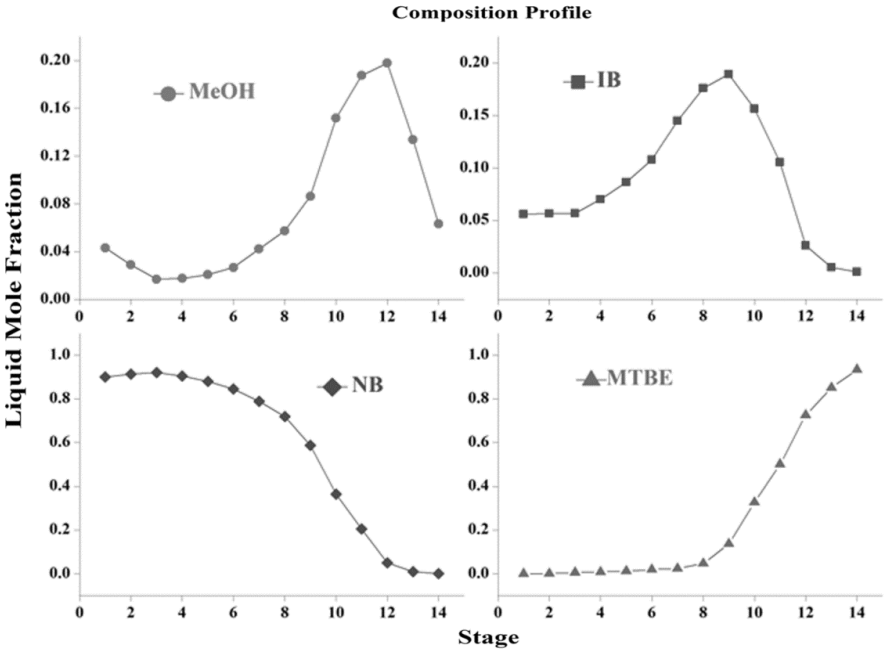

Fig. 4 — Concentration profile in reactive distillation column

Table 4 — Design parameters of reactive heat integrated distillation column

Column Configuration		Feed Specification					
		Stripping Column			Rectifying Column		
Bottom flow rate (kmol/hr)	640.8	Parameter	Methanol	Butene	Parameter	Methanol	Butene
Reflux ratio	7	Feed stage	3	4	Feed stage	4	
Nos. of trays			Reactive: 02 Total: 08		Total: 08		
Feed pressure (atm)	11	Feed temperature (K)	320	350	Bottom flowrate (kmol/hr)	153.2	
Pressure drop (atm)	0.5	Column pressure (atm)	9		Column pressure (atm)	12	
Liquid hold up (m^3)	3	Mole flow (kmol/hr)	711.3	1965.8	Reflux ratio	7	
Number of reactive Trays	2	Composition	1	Iso-butene: 0.36 n-butene: 0.64	Mole flow (kmol/hr)	Top Product from Stripping Column	

the butene mixture is fed. By feeding the recycle stream at 5th stage the forward reaction enhances due to increase in concentration of isobutene which was consumed in the reaction from the above stage. Reaction occurs at 3rd and 4th trays in r-HIDiC. The no. of trays has been selected so that more and more forward reaction can occur to achieve maximum conversion of reactants and obtain high purity MTBE as product.

In this work, the mixed butene fed to the column consists of isobutene and *n*-butene. The bottom product in r-HIDiC column is MTBE as in the case of conventional reactive column. Based on Fig. 5, the pressure difference between the rectifying and striping sections in the r-HIDiC column improves the component concentration in the product streams of the separation process, because the r-HIDiC column works as a type of pressure-swing process. Figure 5 shows the T-x-y diagram for MTBE/Methanol at the pressure operation of r-HIDiC column: 9 atm for the stripping section and 13atmfor the rectifying section. It can be seen that the methanol composition of the azeotrope decreases as the pressure increase.

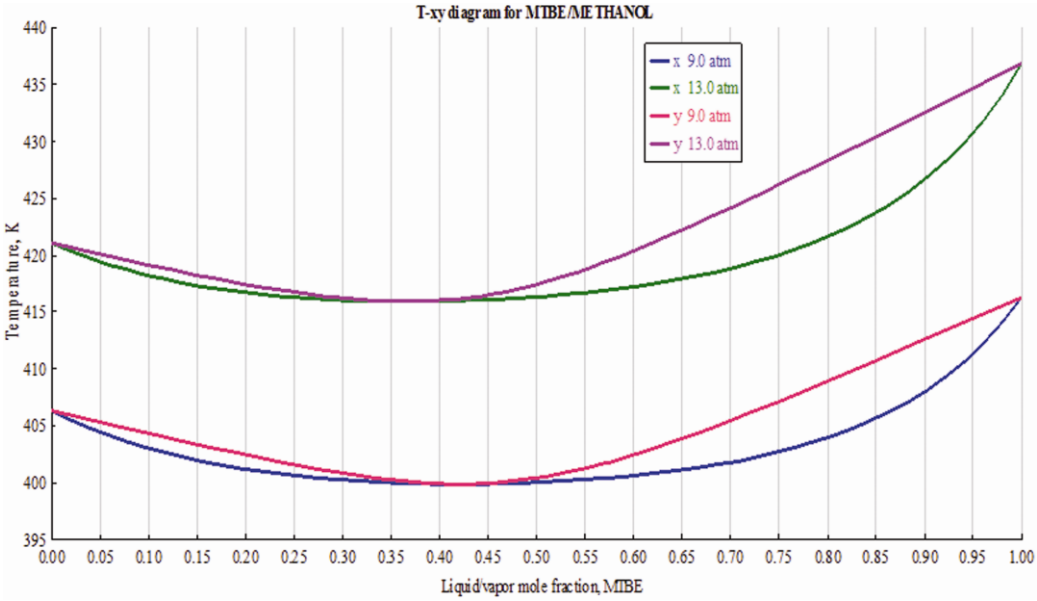

Fig. 5 —T-xy diagram of MTBE/MeOH mixture

Table 5 — Comparison of simulation results for operating conditions, feed and product Flow compositions of RDC and r-HIDiC

		r-HIDiC		*RDC*	
Quantity	*Units*	Top Rectifier	Bottom Stripper	Top	Bottom
x_{MeOH}		0.0943	0.0004	0.049	0.0018
x_{IB}		0.0896	0.0099	0.055	0.000
x_{MTBE}		0.000	0.9447999	0.000	0.987
$x_{n\text{-butene}}$		0.8160	0.0412	0.890	0.00016
Temperature, *T*	K	350.83	406.42	347.22	427.25
Product Flow	kmol/h	1530.38	600	1406.13	640.8
IB conversion	Mole %	96.32		97.95	
MTBE Purity	Mole %	94.53		98.70	

Table 5 shows the results of the heat integrated reactive distillation model. From the Table 5 it can be reported that the bottom product consist of about 0.0018 mol % methanol in reactive distillation column and 0.0004 mol % methanol in the heat integrated reactive distillation. This reduction of methanol composition in case of r-HIDiC is because the reactive stripping section in r-HIDiC is operated at a temperature so as to avoid the existence of azeotrope between product MTBE and methanol. Moreover, there was an increment in concentration of n-butene in bottoms of the reactive stripping section. This may be due to the recycling of bottom stream from rectifying section consisting of n-butene.

Figure 6 shows the temperature profile of r-HIDiC in reactive stripping section of the column. The temperature at the last stage of the stripping section in r-HIDiC is 406 K while that of the stripping section in RDC is 427.24 K. This reduced temperature decreases the composition of methanol in bottom product in stripping column in case of r-HIDiC as methanol forms a homogenous azeotrope with MTBE at 408.53 K. This eliminates the chances of formation of pseudo-aeotrope as it is in the case of RDC[14].

Similarly, as in the case of rectification section in r-HIDiC, the temperature profile is as shown in the Fig. 7. The top product of rectification column separates out the inert *n*-butene from the vapour mixture of stripping column.

The r-HIDiC stripping column composition profiles are shown in Fig. 8. The compression ratio between stripping and rectifying section is 9:13, respectively. This configuration permits to obtain a bottom purity of 95 mol % MTBE in the stripping section. In the distillate of the same reactive stripping section, *n*-butene was obtained at 84 mol %.

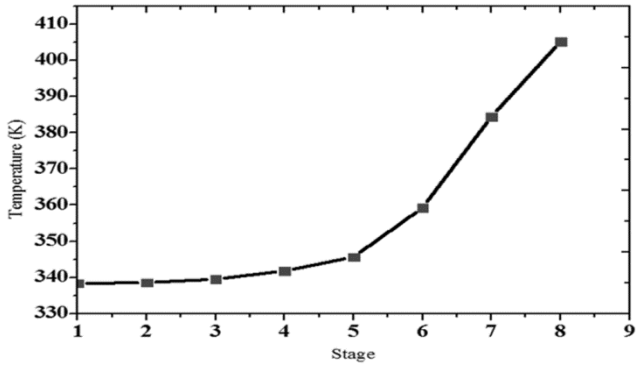

Fig. 6 — Temperature profile in r-HIDiC stripping section

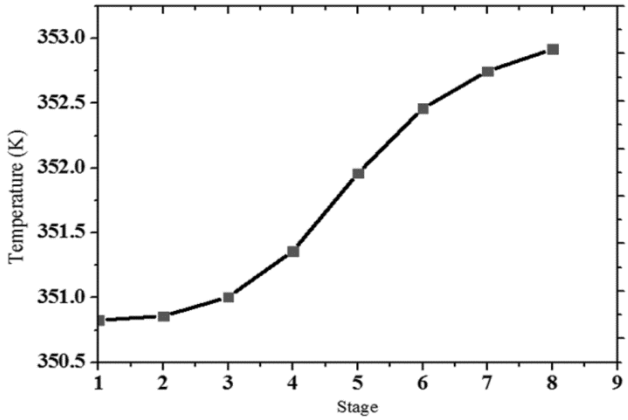

Fig. 7 — Temperature profile in r-HIDiC rectification section

Figure 9 shows the composition profile of rectifying section in r-HIDiC model. In this case, the composition of methanol in the top stage of the column is high as compared to that of the top product composition of RDC column rectifying section. This is due to the fact that methanol conversion in case of r-HIDiC is high as compared to RDC.

Figure 10 displays the total annualized cost (TAC) of this process at different value of compressor ΔP. It can be seen from this figure that the TAC decreases as the compressor ΔP value increases. The top section pressure of stripping column in r-HIDiC is at 9 atm. The compressor work required to increase the pressure of the rectifying column depends on the column pressure to effectively break the azeotrope of MTBE/Methanol. Also, the value of TAC at higher ΔP value decrease because of the fact that the heat duty on both condenser and reboiler decreases for higher compression ratio. Hence, the optimum compression ratio of 9:13was implemented for this model. At this compression ratio, the condition for the formation of pseudo-azeotrope was reduced and the duties to synthesize MTBE were also reduced.

The reaction chemistry for the MTBE process also involves an undesirable reversible reaction that produces methanol and isobutene. To achieve a higher concentration of the product MTBE at bottom section

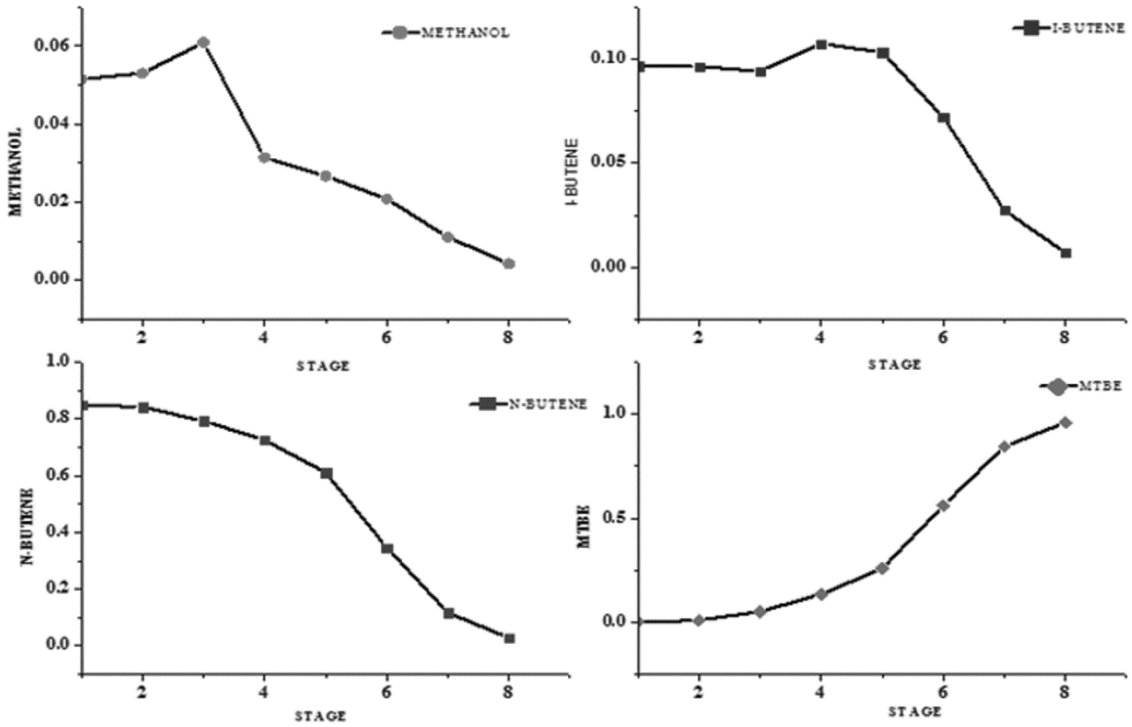

Fig. 8 — Composition profile in r-HIDiC stripping section

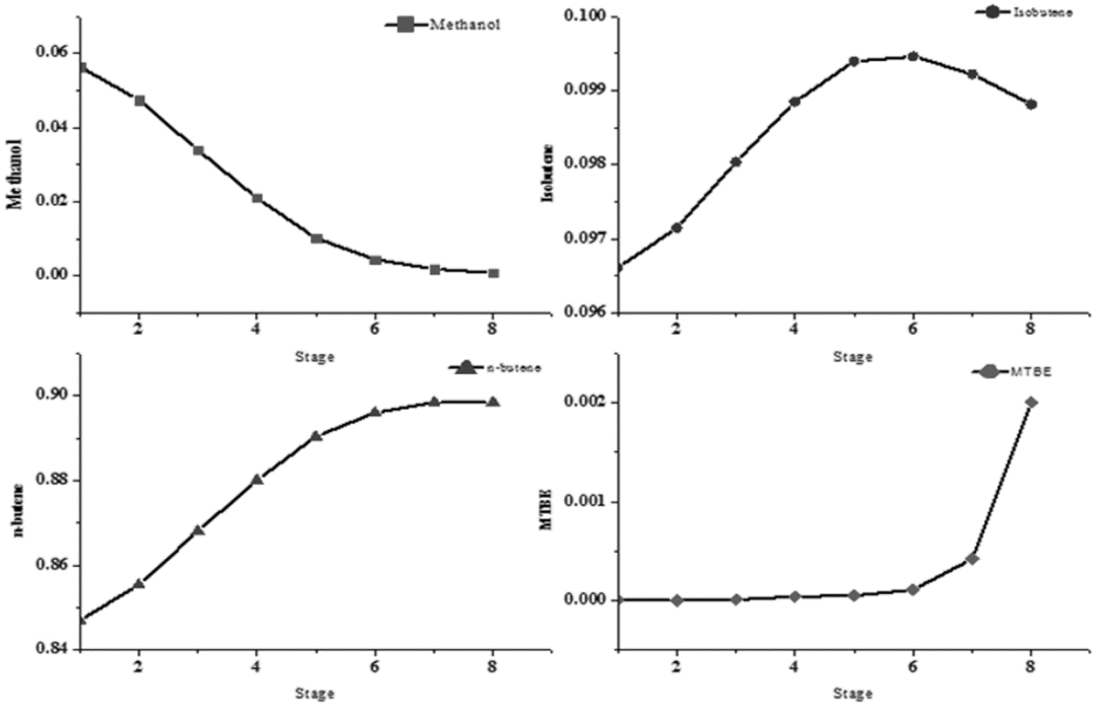

Fig. 9 — Composition profile in r-HIDiC rectification section

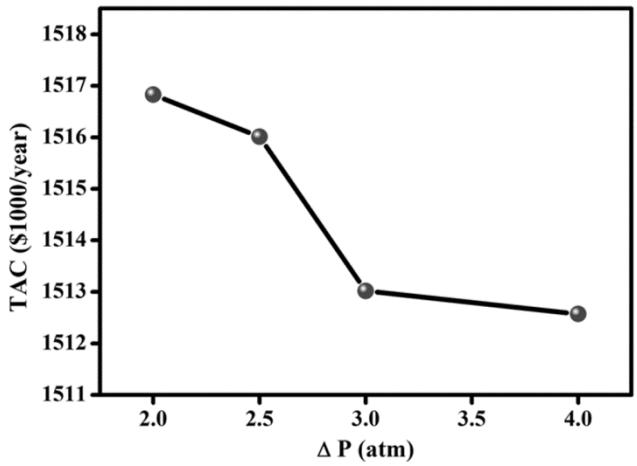

Fig. 10 — TAC versus Δ*P* for the r-HIDiC design.

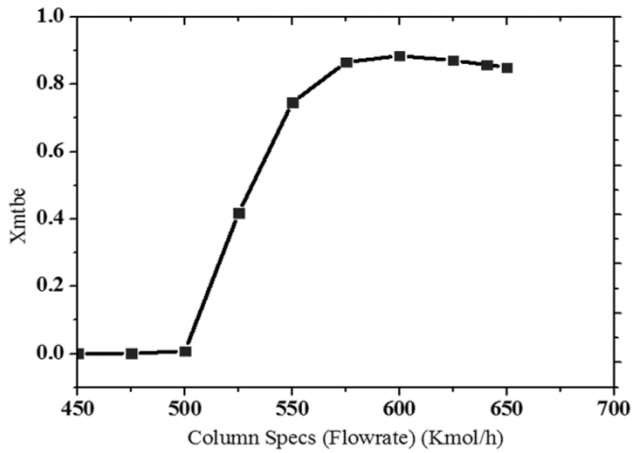

Fig. 11 — Sensitivity analysis results for x_{MTBE} versus bottom flowrate for the r-HIDiC design.

of reactive stripping column, the bottoms flowrate is adjusted to give maximum desired product. The optimum value of bottom flowrate in stripping section of r-HIDiC is set using the sensitivity option of model analysis tool in Aspen plus. The block variable bottom flowrate in column specification is varied within the range of 300-650 kmol/hr. The corresponding composition of MTBE is taken at each flowrate within the given range. The result demonstrates that at 600 kmol/hr maximum concentration of MTBE is achieved. The sensitivityanalysis result is demonstrated in Fig. 11.

Comparative analysis of RDC and r-HIDiC

As can be seen in Table 6, the r-HIDiC presents a decrease in the energy consumption in comparison with a conventional reactive distillation column. However, due to additional load of compressor used in r-HIDiC design and in turn higher operating costs; the additional $215,020 cost is incurred per year. Thus the total annualized cost of heat integrated reactive distillation column is 16.56% higher than that of reactive distillation column design. But the reduction in reboiler and condenser duties is 35.06

Table 6 — Comparison of TAC and heat duties of RDC and r-HIDiC

Parameter	RDC	r-HIDiC	% reduction
TAC ($1000/year)	1298.00	1513.02	-16.56
Reboiler duty (MW)	76.64	49.764	35.06
Condenser duty (MW)	93.76	59.395	36.65

and 36.65% respectively, if heat integration is applied to the reactive distillation column.

Conclusion

In this work, simulation studies are developed in order to specify the feasibility for the implementation of new technology, reactive distillation with internal heat integration, r-HIDiC column. Very few studies about this technology are available in the open literature. This intensified process merges the reactive distillation principles with heat integration techniques in distillation process for MTBE synthesis. The simulations are performed using the commercial simulator ASPEN Plus v8.8.

From the results, the r-HIDiC column shows a reduction in the energy consumption of the order of approximately 36.0 % in relation to the conventional reactive column. The application of r-HIDiC column in the MTBE process presents great advantage for azeotropic separation, owing at the difference of operation pressure in the two section of the r-HIDiC column, increasing the possibility to obtain maximum methanol conversion. The reaction takes place in the stripping section, which allows to the take advantage of heat present in the rectifying section, reducing the power consumption required by the reboiler. It was demonstrated that internal arrangements in distillation process is really effective for process intensification. Not only can product concentration be improved substantially, but the capital investment can also be further reduced.

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